

Thoughts about Density Functional Theory in 1998

WALTER KOHN

Thirty-four years after its beginning, density functional theory (DFT) continues to evolve vigorously. Where initially there was widespread skepticism that *any* theory based on as simple a quantity as the density distribution, $n(r)$, could be of much utility, the record since then has demonstrated its value for many and large classes of systems in physics and chemistry. In 1998, even many of its committed critics have recognized that, at the very least, DFT provides important new viewpoints concerning the electronic structure of matter.

Some quantum chemists see orbitals (especially the Hartree–Fock orbital) as the very essence of their discipline and regard DFT as a mere numerical technique, which may provide good numbers but does not enhance scientific insight. This is no doubt the case for some DFT calculations and is regrettable. But let us not either totally dismiss the value of good numbers for complex and practically important questions. Furthermore, especially in the hands of Robert Parr and his collaborators, DFT has shed some important light on significant chemical concepts such as electron affinity and hardness. Finally, I would like to comment that DFT, in the Kohn–Sham form, involves both density and orbitals, the latter having the advantage that they give rise, at least in principle, to the actual, physical density distribution.

I see DFT as a significant *addition* to other points of view and techniques (and often—as in the case of systems of very many atoms—“the only game in town,” at least at present). Thus, for example, DFT has put a spotlight on the exchange

correlation hole $n_{xc}(r; r')$, which is certainly best thought about in coordinate space, rather than in terms of orbitals, and, along with $n(r)$, provides very useful and suggestive insights into the nature of electronic structure.

DFT is a curious science. The fundamental Hohenberg–Kohn lemma that a finite system with an isolated electronic ground state is completely defined by its ground-state density $n(r)$ is rigorous. But, of course, DFT has gone far beyond this, and in so doing has become both much more useful and also less secure. I have colleagues who will emphasize systems where DFT fails, or at least is suspect—for instance, spin liquids, quantum Hall systems, Mott insulators, etc. They are right that DFT should not be oversold. But neither should one ignore its broad usefulness or stop trying to widen its scope.

Where DFT has problems, such as systems with hybridized localized and delocalized states, or reaction barrier energies, I believe there are needs and opportunities for conceptual, mathematical, and practical progress and I trust that some will be reported in the present issue of this journal.

To make sweeping prognostications for the next decade or century would of course be foolish. But, for what it is worth, I record my own current areas of interest: incorporation of polarization energies into DFT for atoms and molecules at arbitrary distances; the nature of electronic structure near electronic *edges*; and the Mott insulator problem.

I look forward to seeing the new work collected in this special issue.